

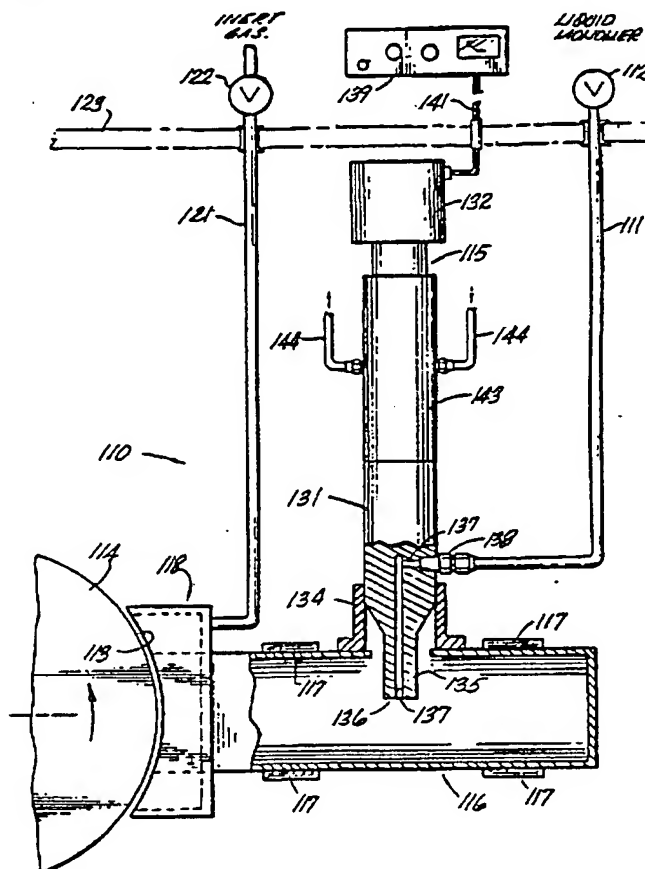


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<b>(21) International Application Number:</b> PCT/US87/01455 <b>(22) International Filing Date:</b> 23 June 1987 (23.06.87) <b>(31) Priority Application Number:</b> 877,175 <b>(32) Priority Date:</b> 23 June 1986 (23.06.86) <b>(33) Priority Country:</b> US  <b>(71) Applicant:</b> SPECTRUM CONTROL, INC. [US/US]; 2185 West Eighth Street, Erie, PA 16505 (US). <b>(72) Inventor:</b> YIALIZIS, Angelo ; 9095 North Oracle Road, No. 1205, Tucson, AZ 85704 (US). <b>(74) Agent:</b> DALY, Thomas, J.; Christie, Parker & Hale, P.O. Box 7068, Pasadena, CA 91109-7068 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** FLASH EVAPORATION OF MONOMER FLUIDS**(57) Abstract**

A method for continuously supplying a uniform vapor of a polymerizable and/or cross-linkable material. A continuous liquid flow of said material is supplied at a temperature below both the decomposition temperature and the polymerization temperature of said material and atomized into a continuous flow of liquid droplets having a particle size from about 1 to about 50 microns. The droplets are continuously vaporized upon contact with a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing. The vapor may be deposited onto a substrate and subsequently polymerized or cross-linked.



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## FLASH EVAPORATION OF MONOMER FLUIDS

Field of the Invention

The present invention relates to a method for depositing a liquid film on a substrate and, more particularly, to a method for depositing a monomeric film on a substrate. Such a film may be polymerized or cross-linked to form a polymeric layer on said substrate.

Cross-References

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This invention is related to the following copending, commonly assigned, U.S. patent applications and patents: Serial No. 620,647, filed June 14, 1984, entitled "Miniaturized Monolithic Multi-layer Capacitor and Apparatus and Method for Making"; Patent No. 4,499,520, issued February 12, 1985, entitled "Capacitor with Dielectric Comprising Poly-Functional Acrylate Polymer and Method of Making"; Patent No. 4,490,774, issued December 25, 1984, entitled "Capacitors Containing Polyfunctional Acrylate Polymers as Dielectrics"; Patent No. 4,533,710, issued August 6, 1985, entitled "1,2-Alkanediol Diacrylate Monomers and Polymers Thereof Useful as Capacitor Dielectrics"; Patent No. 4,513,349, issued April 23, 1985, entitled "Acrylate-Containing Mixed Ester Monomers and Polymers Thereof Useful as Capacitor Dielectrics"; Patent No. 4,515,931, issued May 7, 1985, entitled "Polyfunctional

1 Acrylate Monomers and Polymers Thereof Useful as Capacitor  
Dielectrics"; Patent No. 4,586,111, issued April 29, 1986,  
entitled "Capacitor with Dielectric Comprising a Polymer of  
Polyacrylate Polyether Pre-Polymer"; Serial No. 668,918,  
5 filed November 6, 1984, entitled "Atomizing Device for  
Evaporation"; and Serial No. 692,746, filed January 18,  
1985, entitled "Monomer Atomizer for Evaporator"; all of  
which are hereby incorporated by reference.

10 Background and Objects of the Invention

Various industries require the ability to place thin  
coatings of polymeric materials onto selected substrates.  
One such industry is the electronics industry, especially  
the portion thereof which is concerned with the manufacture  
15 of polymer monolithic capacitors. Other industries which  
rely on the production of thin polymeric coatings on  
various substrates include magnetic tape manufacturers and  
producers of packaging films.

Capacitors are used in a wide variety of electrical  
circuits, for example, in relatively high voltage AC power  
20 systems (such as the common 110-volt systems) and in  
relatively low voltage (e.g., under 50 volts) DC systems  
frequently encountered in printed circuits and the like.  
Important factors which must be considered in the  
manufacture of such capacitors are volumetric efficiency,  
25 temperature of operation, dissipation factor, especially in  
AC systems, and behavior upon failure.

The development of electronic devices and circuits of  
reduced size has led to a need for significantly smaller  
capacitors having increased volumetric efficiency, or  
30 capacitance per unit volume. The polymer-monolithic  
capacitor has been used for such applications.

A monolithic capacitor is one in which the layers of  
electrodes and dielectric are bonded together in a unitary  
structure as opposed, for example, to a metallized film  
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1 capacitor in which self-supporting films are rolled or  
wound into the capacitor form. A miniaturized capacitor is  
one of very small dimensions, so as to be suitable for  
microcircuitry. Small overall size could denote low  
5 capacitance of little practical value, except that the  
thickness of the intervening dielectric layer inversely  
affects the capacitance between adjacent electrodes, and  
the number of electrode pairs and dielectric constant of  
the dielectric directly affects capacitance. Therefore, as  
10 a matter of basic capacitor theory, a capacitor having very  
thin dielectric layers, and many pairs of electrodes or a  
given capacitor with a dielectric having a high dielectric  
constant could have substantial capacitance despite being  
of miniature size with the active area of the electrodes  
being quite small.

15 One such type of polymer monolithic multi-layer  
capacitor is described in application Serial No. 620,647,  
cross-referenced herein. That capacitor has a  
capacitively active section, and two electrode joining  
20 sections, each separated from the active section by a  
sloping section. The capacitor includes a first and second  
set of electrode layers interleaved with one another, each  
layer of each set having an active area extending through  
and contributing to the capacitively active section of the  
25 capacitor in a stacked and spaced apart relationship with  
the active areas of all of the other layers. The electrode  
layers are joined at the margin in stacked electrically  
contacting relationship and each layer has a sloped portion  
between its active area and its margin which contributes to  
30 a sloped section of the capacitor. A dielectric coating is  
in contact with and between each adjacent electrode pair.  
The dielectric coating has a substantially uniform  
thickness in the capacitively active section and tapers to  
zero thickness through the sloping section.

35 The volumetric efficiency of a capacitor, including

1 the monolithic multi-layer capacitor described above, is  
normally measured in terms of capacitance per unit volume.  
Generally, high efficiency is desirable, with values of at  
least about one-tenth (0.1) microfarad per cubic millimeter  
5 for a 50 VDC rated unit being preferred.

As noted above, the volumetric efficiency of the  
capacitor may be increased by reducing the thickness of the  
dielectric layer and/or by increasing the number of  
electrode pairs, both of which may have limits depending  
10 upon the capacitor type and its end use.

From the foregoing, it is evident that in order to  
achieve the results which are desired in accordance with  
the aforementioned application Serial No. 620,647, a method  
for depositing a thin uniform monomeric layer on the  
desired substrate is absolutely essential. Heretofore, it  
15 has been known generally in the art that monomeric layers  
may be deposited upon substrates. For example, U.S. Patent  
No. 3,547,683 and the British counterpart thereof, No.  
1,168,641 deal with the vapor deposition of a polymerizable  
or cross-linkable material which has a vapor pressure under  
20 standard temperature and pressure conditions of less than 1  
Torr. It appears that the concept embodied in such patents  
is simply to allow a heated container of the material to  
vaporize the desired polymerizable or cross-linkable  
material. Such an approach suffers from the fact that by  
25 maintaining a polymerizable or cross-linkable material at  
an elevated temperature for any substantial length of time  
gives rise to the possibility of degradation and/or  
polymerization of the material, within the container, both  
of which are undesirable.

30 U.S. Patent Nos. 4,121,537 and 4,207,836 are both  
concerned with the vapor deposition of a layer of a  
compound consisting of two or more kinds of elements such  
as Se, Te or As through flash evaporation, as by dropping  
raw material, bit-by-bit, into a boat heated to a high  
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1 temperature with the individual bits being vaporized within  
a short time. Thus, the approach of using flash  
evaporation is not taught in said patents to relate to  
monomeric materials as used in the present invention. A  
5 problem with such an approach, as taught in said patents,  
of course, is that as each drop is vaporized, a burst of  
vapor is produced, followed by an intermittent period of  
time during which no vapor is present. Under such  
conditions, it is difficult to achieve a uniform layer of  
10 material on the desired substrate. The foregoing is  
especially true if the source of the vapor and the  
substrate are moving in relation to each other.

U.S. Patent No. 4,153,925 is concerned with the use of  
electron bombardment or ultraviolet radiation of an organic  
monomer to make a dielectric layer, generally. However,  
15 there is no specific teaching regarding the method by which  
the monomer is placed on the desired substrate. Likewise,  
U.S. Patent Nos. 4,277,516; 4,301,765 and 4,378,382 deal  
with the glow polymerization of monomers, without any  
specific indication of how one might achieve a desired  
20 uniform monomeric layer. It is believed that the monomers  
which are glow polymerized and to which those patents  
relate, are monomers which are typically present under  
standard temperature and pressure conditions as a gas and  
thus do not present the same problem as do monomers which  
25 are typically used as liquids.

Thus, especially in view of the process disclosed in  
the aforementioned application, Serial No. 620,647, there  
exists a need for a method by which polymerizable and/or  
cross-linkable materials may be uniformly deposited upon a  
30 desired substrate in a controlled manner such that said  
materials may be subsequently cured to form a desired  
polymeric layer on said substrate. More generally, a need  
exists for a method by which materials may be quickly and  
uniformly deposited upon a desired substrate.  
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Summary of the Invention

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Generally, the present invention provides a method for depositing onto a substrate a layer of material, which may be a polymerizable and/or cross-linkable material, said material being characterized by the fact that it is chemically unstable at or below its boiling point, said method comprising vaporizing said material by continuously placing droplets of said material into contact with a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing; maintaining at least a portion of said substrate at a temperature which is below the boiling point of said material and in a region which is at a lower pressure than said vaporized material, to provide a positive flow of vaporized material toward said substrate; and directing the flow of vaporized material onto said substrate in a predetermined manner.

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In accordance with the present invention, there is also provided a method for continuously supplying a uniform vapor of a material, which may be a polymerizable and/or cross-linkable material, said method comprising supplying a continuous liquid flow of said material at a temperature below both the decomposition temperature and the polymerization temperature of said material, continuously atomizing the liquid flow into a continuous flow of airborne liquid droplets having a particle size from about 1 to about 50 microns, and continuously vaporizing said liquid droplets by causing said droplets to contact a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing.

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The present invention thus also provides a method for

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1 depositing a layer of a material, which may be a  
polymerizable and/or cross-linkable material, on a  
substrate comprising supplying a continuous liquid flow of  
5 said material at a temperature below both the decomposition  
and the polymerization temperature, if any, of said  
material; continuously atomizing said liquid flow into a  
continuous flow of liquid droplets having a particle size  
from about 1 to about 50 microns; continuously vaporizing  
10 said liquid droplets by causing said droplets to contact a  
heated surface which is maintained at a temperature at or  
above the boiling point for said material but below the  
temperature at which said droplets would undergo pyrolysis  
before vaporizing; maintaining at least a portion of said  
15 substrate at a temperature which is below the boiling point  
of said material and in a region which is at a lower  
pressure than said vaporized material, to provide a  
positive flow of vaporized material toward said substrate;  
and directing the flow of vaporized material onto said  
substrate in a predetermined manner.

20 From the foregoing, it should also be apparent that  
when the material is polymerizable and/or cross-linkable,  
by employing the additional step of polymerizing or cross-  
linking the material on said substrate, a method is also  
provided for depositing a polymeric coating on at least a  
25 portion of the desired substrate.

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1     Brief Description of the Drawings

      Fig. 1 is a schematic perspective of an apparatus useful in the practice of the method of the present invention;

5       Fig. 2 is an enlarged fragmentary section of a portion of the apparatus shown in Fig. 2 illustrating the operating phenomenon created;

      Fig. 3 is a top view, with a portion sectioned, of the structure shown in Fig. 2;

10       Fig. 4 is similar to Fig. 3 but illustrates the droplet dispersion resulting from operation of the apparatus;

      Fig. 5 is a schematic partially sectioned apparatus embodying an atomizer useful in performing the process in accordance with the invention; and

15       Fig. 6 is a schematic of an apparatus used to manufacture polymer monolithic capacitors, employing the method of the present invention.

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1     Detailed Description of the Preferred Embodiments

As discussed, the present invention provides a method for depositing a uniform film of a polymerizable and/or cross-linkable material onto a substrate. The polymerizable and/or cross-linkable material may be referred to hereinafter as a monomer or monomeric material. However, as will be detailed below, the material may itself be polymeric in nature.

Thus, the monomers which are useful in the present invention include all such materials disclosed in the cross-referenced applications discussed above, which are hereby specifically incorporated by reference.

In addition, other monomeric materials which are useful in the practice of the present invention include those discussed in U.S. Patent No. 3,547,683, including, but not limited to, low molecular weight addition-type polymers, natural oils, silicone, condensation polymers, and other monomers and materials containing unsaturation which are capable of undergoing polymerization or cross-linking.

From the viewpoint of operability in the present process, any monomer employed herein should either be a liquid at room temperature or should be capable of being converted to a liquid at an elevated temperature, without undergoing any significant decomposition or polymerization. Furthermore, the monomeric materials should have a vapor pressure at standard temperature and pressure, of less than about 1 Torr and preferably less than about  $10^{-3}$  Torr. It is also contemplated that monomers useful in the present invention include those monomers which, although not themselves a liquid at room temperature are capable of being dissolved in other suitable liquids to form an azeotropic solution.

The particularly preferred monomeric materials for use in the present invention are the polyacrylate polyether

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1 prepolymers disclosed in the cross-referenced U.S. Patent  
No. 4,586,111, issued April 29, 1986.

5 The monomers used in the present invention are  
generally characterized by the fact that they are  
chemically unstable at temperatures at or even below their  
boiling point. The term "chemically unstable" is used  
herein to refer to any type of chemical instability,  
including, but not limited to, oxidation or other chemical  
degradation of the monomer as well as the formation of  
10 polymers or oligomers.

As indicated above, the first step in the method of  
the present invention involves continuously supplying  
droplets of the monomer. Such droplets may be produced by  
continuously supplying a stream of the liquid monomer and  
continuously atomizing said monomer into a continuous flow  
15 of droplets which preferably are uniform liquid droplets  
having a particle size from about 1 to about 50 microns.  
Typically, the particle size of the liquid droplets will be  
from about 1 to about 20 microns and most typically will be  
centered around particles having a particle size from about  
20 5 to about 10 microns.

Although, in general, the atomized droplets employed  
in the present process will fall within the size range of  
about 1 to about 50 microns, it is theoretically best to  
25 use the smallest particle size possible. Thus, particles  
of less than 1 micron in size may be advantageously  
employed in the present invention. However, from a  
practical viewpoint, it is not usually possible to atomize  
the monomers into such a fine particle size, so other  
30 considerations must be used to determine the largest  
particle size which will be acceptable.

It is, of course, to be appreciated that when  
discussing the largest particle size employed in any given  
embodiment of the present invention, the actual droplets  
employed will have a particle size distribution range  
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1 peaking at some level significantly below the maximum  
particle size. Thus, for example, in a typical embodiment  
of the present invention the particle size employed may  
range from about 1 to about 20 microns, with the  
5 distribution peak occurring at about 10 microns. As used  
herein, it is to be appreciated that the "particle size" of  
a particle is meant to refer to the diameter of that  
particle.

It should be understood that a principal goal of the  
10 present invention is to achieve vaporization of the monomer  
particles from the heated surface in such a manner that no  
fluid accumulates on said substrate. Thus, to achieve a  
continuous flow of monomer vapor by vaporizing monomer  
droplets from the heated surface, the size of those monomer  
15 droplets typically needs to be such that the vaporization  
of the monomer deposited from each droplet will occur in  
less than about 50 milliseconds, more typically within less  
than about 20 milliseconds, and most typically within less  
than about 10 milliseconds. Ideally, it would be preferred  
20 for the vaporization of the monomer to occur in less than 1  
millisecond. However, practical limitations again usually  
dictate that the vaporization occur in the range from about  
10 to about 20 milliseconds. The actual length of time  
needed for vaporization is, of course, dependent upon many  
25 considerations, besides the size of the monomer droplet.  
Such considerations include the nature of the monomer, such  
as its vapor pressure under standard temperature and  
pressure conditions, the degree of vacuum under which the  
heated surface is placed, and the temperature to which the  
30 surface is heated.

The exact mechanism for atomizing said liquid monomer,  
in general, is not critical and any suitable method may be  
employed. However, for many applications it is critical  
that the method of atomizing said liquid monomer be precise  
35 in that substantially all of the particles fall within the

1 desired size range and that the particles are supplied in a  
continuous flow which is thus not intermittent in nature.  
The need for the continuous flow is evident when  
5 considering the fact that the typical ultimate use may be  
the deposition of a uniform polymer layer as, for example,  
a dielectric coating in a monolithic capacitor structure.

One suitable method for atomizing the liquid monomer  
is disclosed in the cross-referenced application Serial No.  
668,918 and another such method is disclosed in Serial No.  
10 692,746, filed January 18, 1985, entitled "Monomer Atomizer  
for Evaporation".

Employing the apparatus taught in either of the two  
aforementioned applications in the manner described therein  
will result in the generation of monomer particles of the  
15 desired size range, in a continuously flowing, uniform  
stream. Any other device may be employed to atomize the  
liquid monomer, so long as it results in the generation of  
the desired size of particles in a uniform, continuous  
flow.

20 With respect to the step of vaporizing the liquid  
droplets, again, any suitable heated surface may be  
employed. The temperature of the heated surface should be  
such that vaporization occurs instantaneously upon contact  
with the surface by the monomer droplets. However, the  
25 temperature should also not be so high as to cause  
pyrolysis of the material, that is to cause oxidation or  
other degradation of the monomer structure itself.

With respect to the physical form of the heated  
surface, any desirable shape may be employed. Various  
30 structures are shown in the cross-referenced applications.  
It is usually desirable for the heated surface to be  
contained in or to actually form a vaporization chamber in  
which the liquid droplets may be vaporized. Such a chamber  
may also define a means for directing the flow of monomer  
35 vapor onto a substrate. In such an embodiment, the chamber

1 may terminate in the form of a flow directing means, or  
nozzle, such that the liquid monomer droplets upon being  
vaporized create an internal pressure within the chamber  
causing the monomer vapor to be expelled out the nozzle or  
5 other flow directing means in the direction of the  
substrate.

In the manufacture of monolithic capacitors, the  
preferred substrate is a copper sheet. As may be  
appreciated, in the manufacture of monolithic capacitors,  
10 the copper sheet may itself be coated with layers of  
polymeric material, alternating with layers of conducting  
material, such as aluminum about 200 to 500 angstroms  
thick. Thus, a typical substrate would be a copper sheet  
on which alternating layers of polymeric material formed  
15 through the method of the present invention and alternating  
conducting layers of aluminum are present.

The substrate itself should be located in a region  
which is maintained at a lower pressure than the pressure  
generated through the vaporization of the monomer droplets.  
20 With respect to the pressure employed as in the manufacture  
of monolithic capacitors, the pressure in the deposition  
zone is usually below 10 Torr, preferably below  $10^{-1}$  Torr  
and advantageously  $10^{-4}$  Torr, or even less.

The layer of film of monomeric material deposited on  
25 the substrate may be any suitable depth. However, the  
depth of the deposited film should usually be such that the  
subsequent means of polymerization or cross-linking will be  
effective in curing the monomeric material throughout  
substantially its entire depth.

30 With respect to the step of polymerizing the deposited  
film, any suitable methods may be employed. Thus, thermal,  
electron beam, or ultraviolet radiation curing may be  
employed, depending upon the nature of the monomer. A  
particularly suitable method for curing employs the use of  
35 a beam of accelerated electrons whose energy is generally

1 up to about 20 kev, as are available from conventional  
electron accelerators. The energy of the irradiation and  
the length of time for which the monomeric film is exposed  
to the radiation should be such as to polymerize or cross-  
5 link the material throughout its thickness. The present  
invention, in its preferred embodiments, may be further  
appreciated by reference to the drawings and the following  
description.

Two different apparatus have been developed for flash  
10 vaporizing a liquid according to the present invention.  
These apparatus will now be described in detail. It is to  
be understood, however, that these apparatus are not the  
only apparatus which can be used in practicing the present  
invention. Any apparatus capable of continuously atomizing  
15 a liquid to the appropriate particle size and continuously  
vaporizing the liquid particles in contact with a heated  
surface could be used to advantage in the present  
invention.

Turning to Fig. 1, there is shown a first embodiment  
20 of an apparatus 10 for vaporizing a liquid, such as a  
monomeric resin, supplied in a reservoir 11 and depositing  
by condensing the resulting vapor on a substrate 12  
arranged to move past the apparatus 10. It will be  
understood that both the apparatus 10 and the substrate 11  
25 are maintained in a low vacuum environment. The intent of  
the vapor deposition is to deposit a uniform, very thin--  
one micron or less -- coating of the liquid material on the  
substrate 12.

The apparatus includes a vaporization chamber 13  
30 formed with a nozzle opening 14 for emitting the vaporized  
material in close proximity to the substrate 12. The  
chamber 13 encloses a spinning disk 15 driven by a motor 15  
which throws by centrifugal force atomized droplets of  
fluid against a band heater 17 defining a heating surface  
18 surrounding the disk 15. The tiny droplets are flash  
35

1 vaporized upon contact with the heated surface 18, thereby  
developing both vapor and vapor pressure to expel the  
gaseous material through the nozzle opening 14 for  
condensation on the substrate 12. When the fluid is a  
5 monomeric liquid, the flash vaporization preserves the  
chemical structure, and the condensed monomer film on the  
substrate can be later cured, if desired, by any suitable  
technique such as applying ultraviolet or electron beam  
radiation.

10 In accordance with the invention, the atomizing device  
includes, in addition to the driven disk 15, a capillary  
tube 20 mounted on the reservoir 11 for delivering fluid at  
right angles to the flat circular face 21 of the disk 15,  
and the end of the tube 20 is spaced from the face 21 so  
15 that a liquid drop formed at the tube end is just contacted  
by the face. With the proper spacing, disk face speed and  
drop size, the face rotates the drop as shown in Fig. 2  
while pulling a fluid film on the face 21 free from the  
drop, which fluid film is continuously replenished from the  
20 tube 20, and the film is thrown centrifugally in atomized  
droplets having a particle size from about 1 to about 20  
microns, from the periphery of the disk onto the heated  
vaporizing surface 18. The droplets will be thrown from  
the disk surface 21 along the path lines 22 illustrated in  
25 Fig. 4.

30 If the tube 20 is initially positioned near the center  
of the spinning disk 15 and then moved peripherally outward  
so as to gradually increase the speed of the surface  
contacting the drop, the condition described above and  
illustrated in Fig. 2 will be reached. Representative  
relationships found suitable for a monomeric liquid resin  
included a 20 mil capillary tube feeding liquid to a disk  
1" in diameter driven in the 3,000 to 5,000 rpm range. The  
formed drop, depending upon the liquid's viscosity and  
35 surface tension, contacted the disk with the tube end



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1 spaced about 37 mils from the disk. The disk was formed of  
clean glass. The drop rolling and film forming phenomenon  
was achieved with the spacing 23 (see Fig. 3) of the drop  
from the disk center being about  $3/8$ ". Droplets are  
5 produced and discharged along the paths 22.

While the disk surface 21 has been illustrated as  
horizontal with the tube at a vertical right angle, the  
surface 21 can be disposed vertically and the tube  
horizontal so long as the tube is positioned so that the  
10 drop contacts the upwardly driven half of the disk surface.  
So disposed, the viscosity pull of the disk on the liquid  
counteracts the gravity pull.

The arrangement described produces a continuous rate  
of very low volume droplets well suited for subsequent  
15 flash vaporization and deposition of a very thin coating  
layer. The vapor delivery rate can be increased, if  
desired, by pressurizing the reservoir 11. Liquids of  
varying viscosity would produce initial droplets of varying  
size depending upon the size of the capillary tube, but  
20 the disk and tube relative spacing could obviously be  
readily varied to accommodate varying drop sizes.

Fig. 5 is a schematic partially sectioned apparatus  
embodying a second, and presently preferred, embodiment of  
an atomizer useful in performing the process in accordance  
25 with the invention.

Turning to Fig. 5, there is shown another apparatus  
110 for vaporizing a monomeric liquid supplied through a  
line 111 and valve 112, and vacuum depositing the vapor  
onto a surface 113 carried by a rotating drum 114. The  
liquid is atomized by a structure 115 embodying the  
30 invention, vaporized in a vaporization chamber 116 heated  
by heaters 117, and deposited through nozzle structure 118  
onto the drum surface 113. The nozzle structure 118  
controls the vapor deposition in part by confining vapor  
flow with inert gas, supplied through a line 121 and valve  
35

1 122. The apparatus 110 is mounted within a vacuum chamber  
123.

5 In accordance with this second and preferred  
embodiment, the structure 115 is essentially integrally  
formed with a tip portion 131 at one end extending, and  
delivering liquid, into the vaporization chamber 116 and  
having an ultrasonic vibration device 132 coupled at the  
10 opposite end. The structure 115 is supported by a collar  
134 that closes the chamber opening through which the tip  
portion 131 extends and which is fixed to the tip portion  
at approximately its nodal point. The tip portion 131 has  
a necked-down tip 135 ending in a surface 136 to which the  
15 liquid is directed through a capillary passage 137 in the  
tip portion 131 that is connected to the liquid feed line  
11 by a compression coupling 138. The device 132,  
preferably a piezoelectric crystal transducer, is energized  
by an electronic power supply 139 through a line 141.  
20 Ultrasonic vibration of the tip 135 and its surface 136  
causes the liquid to flow from the passage 137, coat the  
surface 136 and be dispersed in fine droplets through a  
widespread pattern in the chamber 116. The pattern seen is  
in the form of a shallow cone when a substantially flat  
surface like the surface 136 is utilized. Upon striking  
25 the hot chamber walls, temperatures of 350° to 400°F being  
typical, the liquid is vaporized, creating gaseous pressure  
driving the vapor through the nozzle structure 118 so as to  
be deposited on the surface 113.

30 The lengths of the coupling 143 and tip portion 131  
correspond to one-half wavelength of the vibration, and the  
device 132 is operated at their fundamental frequency mode  
with maximum amplitude of motion at the surface 136 and  
minimum movement, or node positions, at the attachment  
points of the coupling 143 and tip portion 131. To protect  
the vibration device 132 from heat, the structure 115  
35 includes a cooling coupling 143 interposed between and

1 rigidly connected to the tip portion 131 and the vibration  
device 132. Cooling water is directed through a passage in  
the coupling 143 using lines 144. The coupling 143 and the  
cooling water absorb and remove heat conducted from the  
5 vaporization chamber 116 along the tip portion 131 so that  
extreme temperatures cannot adversely affect the vibrating  
device 132. To minimize vibration absorption, the lines  
138, 144 and the connection with the collar 134 are located  
at or near the vibration node positions. The structure 115  
10 is left supported cantilever fashion by the collar 134 so  
that the device 132 can vibrate undampened.

It has been found that a material like titanium alloy  
6AL4V is suitable for the tip portion 131. The diameter of  
the passage 137 is dependent upon the flow rate of the  
15 liquid being conveyed through the line 111, and diameters  
of 20 mils to 1/8" have been found suitable.

The basic structure represented by the tip portion  
131, vibration device 132 and electronics 139 can be found  
in standard laboratory equipment such as ultrasonic  
emulsifying devices and this utilization of relatively  
20 standard components makes the atomizer structure economical  
to manufacture and maintain.

Capacitors made using the method of the present  
invention may be formed of materials and in configurations  
known in the art. The conductive materials are typically  
25 aluminum, zinc, alloys of these metals and bi-layers  
involving at least aluminum or zinc and another metal, with  
aluminum being preferred. Aluminum and zinc are unique  
because of their contribution to the self healing  
properties of a capacitor. For example, one embodiment of  
30 the present invention provides a capacitor which includes a  
first electrode which may be, for example, an aluminum  
layer, a dielectric coating of a polymer formed by  
deposition of a monomeric material in solution, on the  
surface of the first electrode by the method of the present  
35

1 invention, followed by polymerization and a second  
electrode which is a second thin metallized layer  
preferably of aluminum deposited on the dielectric film.  
Suitable leads are attached to the first and second  
5 electrodes.

The present invention likewise is useful in the  
manufacture of polymer monolithic multi-layer capacitors  
such as those described and claimed in application Serial  
No. 620,647. Capacitors of this type may be produced by  
10 depositing alternating electrode and dielectric layers so  
as to provide alternate electrode layers with portions  
projecting from the stack and contacting each other in  
electrically connected relation as more fully described in  
that application. The dielectric coating comprises a  
15 polymer which is formed by using the method of the present  
invention to deposit a layer of a monomeric material on the  
electrode and subsequent polymerization of the monomeric  
material. The use of electron beam polymerization is  
particularly preferred because it provides rapid  
20 polymerization of the pre-polymer without the need for  
additional curing agents, and thus leads to economical  
production of very thin coatings.

The method of the present invention wherein the layer  
of monomeric material is deposited on a substrate and  
subsequently polymerized or cross-linked may thus be  
25 employed in the manufacture of polymer monolithic  
capacitors using an apparatus arranged as shown in Fig. 6  
which includes apparatus arranged within and around a  
chamber 230 which is either a vacuum chamber or a housing  
divided into vacuum portions. Within a vacuum environment  
30 is a carrier 231, a dielectric deposit system 232, a  
monomer curing system 233, and an electrode material  
deposit system 234. A substantial vacuum is required down  
to the order of  $1 \times 10^{-4}$  Torr.

35 The carrier 231 is a water cooled drum 235 driven by a

1 motor 236 and whose outer cylindrical surface 237 defines a  
rapidly moving continuous surface passing through a  
dielectric forming zone and an electrode forming zone. The  
regions in which the drum surface 237 and the systems 232,  
5 233 are located constitute the dielectric forming zone, and  
the region in which the drum surface 237 and the system 234  
are located constitute an electrode forming zone. Drum  
rotation creates the machine direction 226, which is the  
direction the surface passes through the dielectric forming  
10 zone and the electrode forming zone.

Because of the small dimensions involved, the surface  
237 should be smooth and true. The sheet of substrate 213  
is firmly secured to the drum 35 and, when in place, the  
outer surface of the substrate defines the surface 237.  
15 The drum 235 is cooled to about 70°F so as to facilitate  
condensation of the vapor deposits, and the apparatus  
functions at drum surface speeds of 150 to 600 feet per  
minute.

The electrode material deposit system 234 includes a  
conventional electron beam vaporization device 241 such as  
20 those used for metallizing film within a vacuum  
environment. The rate of vaporization is sensed by a  
conventional quartz monitoring device 242 providing  
feedback for controlling the rate at which aluminum is  
vaporized by the device 241.  
25

The alternate pattern of metal vapor deposition is  
obtained by shifting the mask 243 axially of the drum 235  
upon each drum revolution. A mask motor 247 makes the  
shifting movement through a simple mechanical connection  
248. A controller 250 is connected to the drum motor 236  
30 for sensing drum revolution, and the controller 250  
supplies the appropriate shifting signal to the mask  
shifting motor 247. It is desirable to keep the mask 243  
close to the surface onto which the metal vapor is being  
deposited, and this closeness is maintained by a mask  
35

1 retraction motor 251 which steps the mask away from the surface 237 upon each drum revolution, as signalled by the controller 250, through a distance approximating the thickness of the electrode layer being deposited.

5 As it is convenient to energize the device 241 and bring it into stable operating condition before beginning to make capacitors, a removable shutter 252 is interposed between the device 241 and the mast 243 for closing off the passage of vapor until the shutter 252 is withdrawn.

10 As a feature of the invention, the dielectric deposit system 232 flash vaporizes the dielectric in monomer form as discussed above in conjunction with Figs. 1 through 5.

15 The condensed liquid monomer is radiation cured by the second system 233 in the dielectric forming zone which includes a radiation source, preferably a gas discharge electron beam gun.

20 The overall operation of the apparatus of Fig. 6 can now be readily understood. Electrode layers are deposited, coated with dielectric and the dielectric cured, before the surface on which the electrode layers are deposited passes again for successive electrode layers and dielectric coatings. Desired thicknesses of the electrode layers and dielectric coatings are determined by matching the rate of vapor deposition with the surface speed of the drum 235.

25 The above description has paid particular attention to application of the method of the present invention in making polymer monolithic multi-layer capacitors. However, the method of the present invention should not be understood as being limited to such an application or even limited to depositing a monomeric film on a substrate for subsequent polymerization and/or cross-linking. The method of the present invention can be used to advantage in any application requiring a controlled supply of vaporized material. For example, if the material to be evaporated is a mixture of components having different vapor pressure,

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1 flash vaporization provides a supply of vapor wherein the  
components are present in the same ratios as in the  
mixture. This would not be true of a supply of vapor  
created by bulk evaporation of the mixture. Thus, flash  
5 vaporization is particularly beneficial in any application  
requiring a controlled supply of a vaporized mixture, such  
as chemical vapor deposition.

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## 1 WHAT IS CLAIMED IS:

1. A method for continuously supplying a uniform vapor of a material, said method comprising:

5 supplying a continuous liquid flow of said material at a temperature below both the decomposition temperature and the polymerization temperature, if any, of said material;

continuously atomizing the liquid flow into a continuous flow of liquid droplets having a particle size from about 1 to about 50 microns; and

10 continuously vaporizing said liquid droplets by causing said droplets to contact a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing.

15 2. The method of claim 1 wherein the liquid droplets have a particle size from about 1 to about 20 microns.

20 3. A method for depositing onto a substrate a layer of material, said material being characterized by the fact that it is chemically unstable at or below its boiling point, said method comprising:

25 vaporizing said material by continuously placing droplets of said material into contact with a heated surface which is maintained at a temperature at or above the boiling point for said material, but below the temperature at which said droplets would undergo pyrolysis before vaporizing;

30 maintaining at least a portion of said substrate at a temperature which is below the boiling point of said material and in a region which is at a lower pressure than said vaporized material, to provide a positive flow of vaporized material toward said substrate; and

35 directing the flow of vaporized material onto said substrate in a predetermined manner.

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4. The method of claim 3 wherein the liquid droplets have a particle size from about 1 to about 20 microns.

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5. The method of claim 3 wherein the substrate is maintained in a region which is at a pressure below about  $10^{-1}$  Torr.

10

6. The method of claim 3 wherein the material is polymerizable and/or cross-linkable and also comprising the step of polymerizing or cross-linking the material on said substrate.

15

7. The method of claim 6 wherein the material is polymerized and/or cross-linked throughout its thickness by use of electron beam curing.

20

8. A method for depositing a layer of a material on a substrate comprising:

supplying a continuous liquid flow of said material at a temperature below both the decomposition and the polymerization temperature, if any, of said material;

25

continuously atomizing said liquid flow into a continuous flow of liquid droplets having a particle size from about 1 to about 50 microns;

30

continuously vaporizing said liquid droplets by causing said droplets to contact a heated surface which is maintained at a temperature at or above the boiling point for said material but below the temperature at which said droplets would undergo pyrolysis before vaporizing;

35

maintaining at least a portion of said substrate at a temperature which is below the boiling point of said material and in a region which is at a lower pressure than said vaporized material, to provide a positive flow of vaporized material toward said substrate; and

1 directing the flow of vaporized material onto said  
substrate in a predetermined manner.

5 9. The method of claim 8 wherein the liquid droplets  
have a particle size from about 1 to about 20 microns.

10 10. The method of claim 8 wherein the substrate is  
maintained in a region which is at a pressure below about  
 $10^{-1}$  Torr.

11 11. The method of claim 8 wherein the material is  
polymerizable and/or cross-linkable and also comprising the  
step of polymerizing or cross-linking the material on said  
substrate.

15 12. The method of claim 11 wherein the material is  
polymerized and/or cross-linked throughout its thickness by  
use of electron beam curing.

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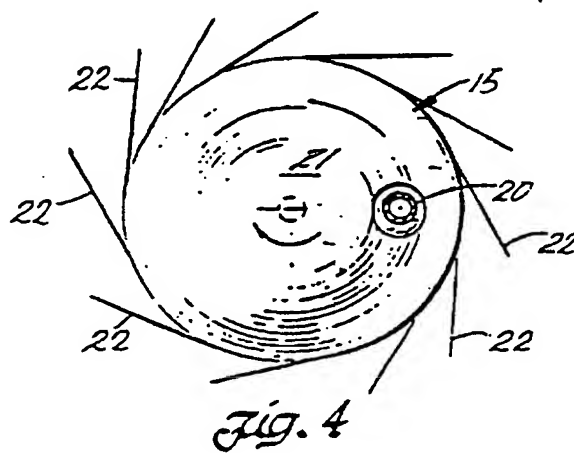
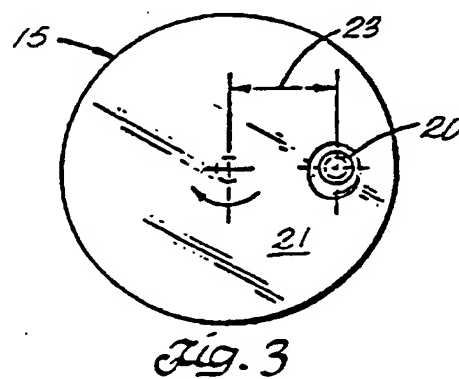
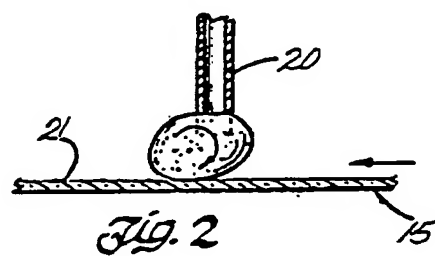
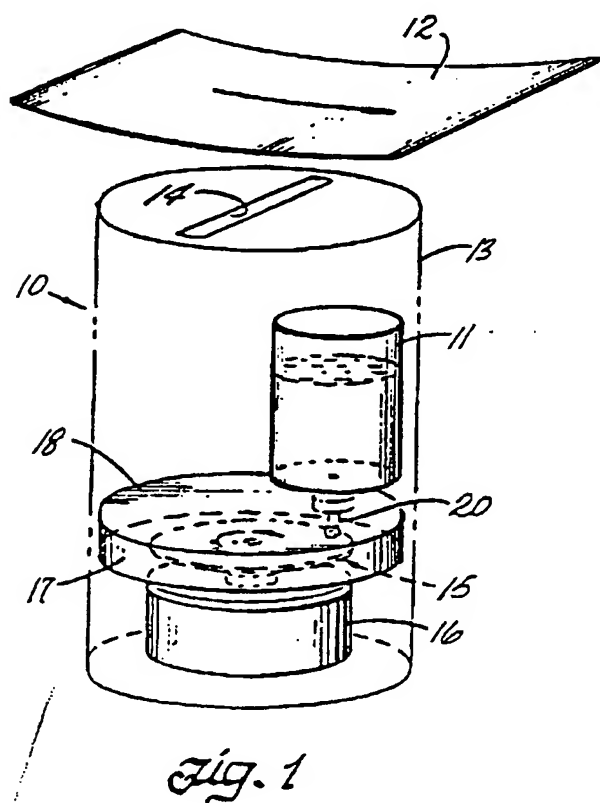
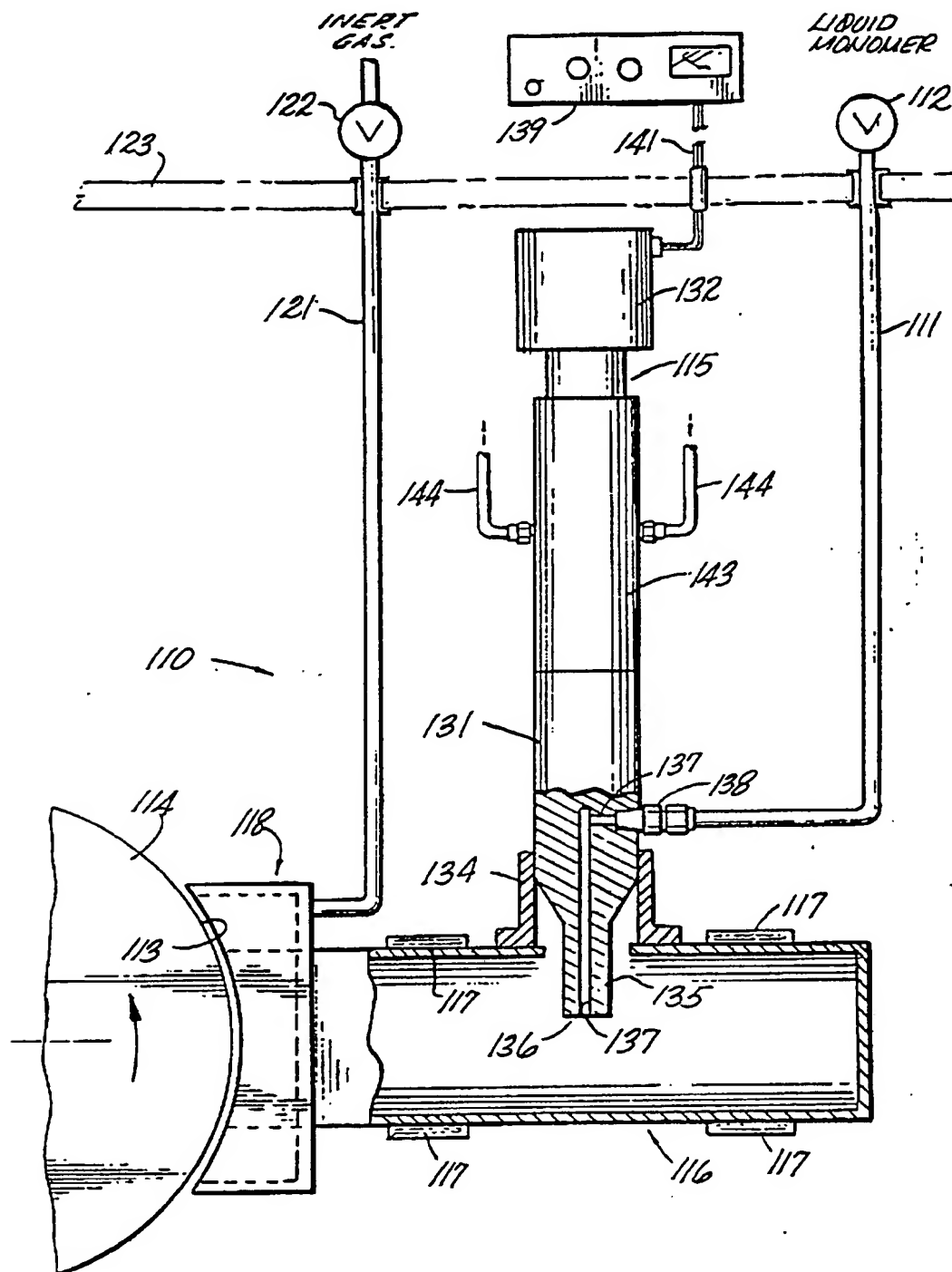
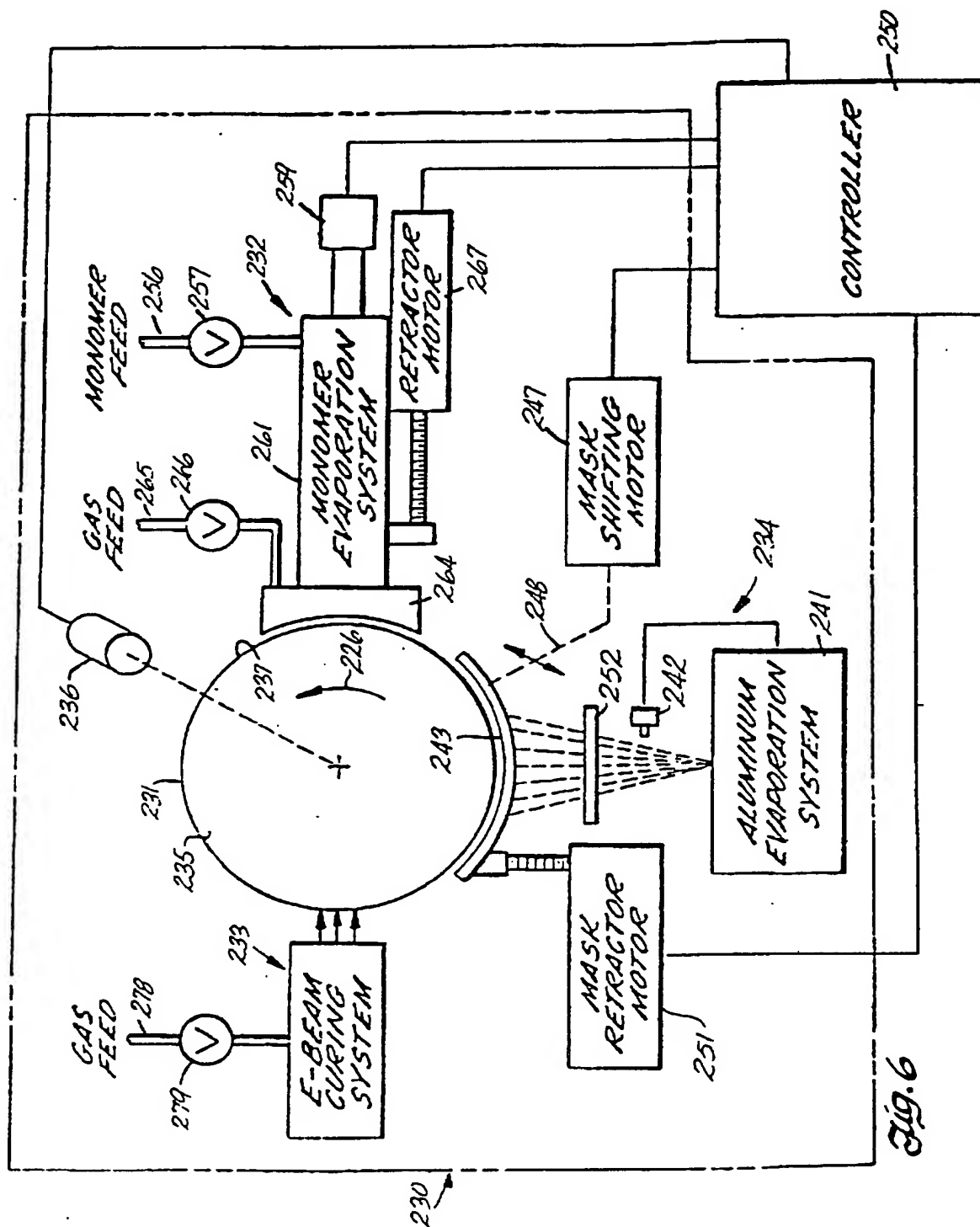


Fig. 5





# INTERNATIONAL SEARCH REPORT

International Application No **PCT/US87/01455**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> : B01D 1/16; B05D 1/02, 5/12; C23C16/00		
US CL 219/273, 275; 427/44, 80, 81, 127, 248.1, 255.6, 421		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
US	219/272, 275; 427/44, 255.6	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>5</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>6</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
Y	US, A, 4,076,866 (PLATAKIS) 28 FEBRUARY 1978, SEE ENTIRE DOCUMENT.	1-12
Y	US, A, 4,543,275 (AKASHI) 24 SEPTEMBER 1978, SEE ABSTRACT AND COLUMN 2, LINES 59 AND 60.	1-12
Y	GB, A, 1,253,124 (DAVIES) 10 NOVEMBER 1971, SEE ENTIRE DOCUMENT.	1-12
Y	JP, A, 59-177365 (MATSUSHITA ELEC. IND KK) 24 MARCH 1983, SEE ABSTRACT.	1-1.2
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>13</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search <sup>1</sup>	Date of Mailing of this International Search Report <sup>1</sup>	
06 AUGUST 1987	31 AUG 1987	
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>19</sup>	
ISA/US	J. A. BELL	

# INTERNATIONAL SEARCH REPORT

Internat. Application No  
PCT/US 96/12288

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B05D7/24 C23C16/44

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B05D C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,87 07848 (SPECTRUM CONTROL INC) 30 December 1987 see the whole document	1
A	US,A,4 696 719 (BISCHOFF GREGG C) 29 September 1987 see the whole document	4,5

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 November 1996

Date of mailing of the international search report

28. 11. 96

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